

"On certain Properties of the Alloys of Silver and Cadmium."

By T. KIRKE ROSE, D.Sc. Communicated by C. T. HEYCOCK,
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[PLATE 10.]

It has long been known that an alloy of silver and copper is not a satisfactory material for the trial plates which are used in testing the fineness of the Imperial silver coin and of silver wares before they are hall-marked. As long ago as the year 1580 the lack of homogeneity of silver-copper alloys was well known to the German metallurgists,* and in 1852 Levol concluded† that the only uniform alloy of the series contained 718·93 parts of silver and 281·07 parts of copper, a composition which corresponds to the formula Ag_3Cu_2 . In 1875 Roberts-Austen, as the result of very carefully conducted experiments,‡ found that under the most favourable circumstances the difference in composition between the centre and corners of a small ingot amounted to 1·2 parts per 1000, and was generally much greater. In 1899 when further attempts were made to prepare ingots of silver and copper of uniform composition,§ similar results were obtained, although many castings were made in accordance with the method recommended by E. Matthey.||

A consideration of the cooling curve of the standard silver-copper alloy, containing silver 92·5, copper 7·5 by weight, which was obtained by Roberts-Austen,¶ and is reproduced in C fig. 1, shows that such segregation must necessarily take place. The initial freezing point d_1 of this alloy, in which the percentage by atoms is silver 87·9, copper 12·1, is at about 900°. At this temperature a solid solution rich in silver begins to crystallise out, but solidification is not complete until the temperature has fallen to 778° (d_2 fig. 1), when the mother liquor contains only 60 atoms of silver to 40 of copper, that is to say, the proportion found by Heycock and Neville to be present in the eutectic alloy.** During the pasty stage ample time is allowed for the segregation of the silver-rich constituent, with the result that the distribution of silver in the solidified metal is not uniform. The amount of segregation varies with the dimensions of the ingot,

* See pp. 20 and 26 of 'Allerfurnemisten Mineralischen Eerzt und Bergwerksarten,' by L. Ercker. Published at Frankfort in 1580.

† 'Ann. de Chimie et de Phys.' (3), vol. 36 (1852), p. 193 and vol. 39 (1853), p. 163.

‡ 'Roy. Soc. Proc.', vol. 23 (1875), p. 481.

§ Thirtieth Annual Report of the Mint (1899), p. 69.

|| 'Roy. Soc. Proc.', vol. 55 (1894), p. 265.

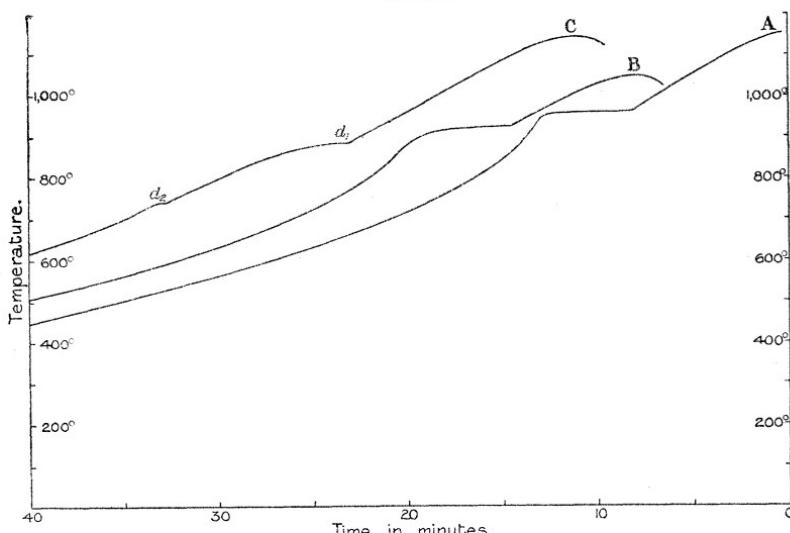
¶ First Report to the Alloys Research Committee, 'Inst. Mech. Eng. Proc.,' 1891, p. 543.

** 'Phil. Trans.,' A, vol. 189 (1897), p. 25.

the shape and temperature of the mould in which it is cast, the temperature of casting, and the rate of cooling. In the case of ingots weighing about 125 ozs. troy (4 kilos.), the ordinary weight of the Imperial trial plates, the centre of the mass is usually richer in silver than the outside to the extent of from 1—3 parts per 1000.

When a pure metal such as silver is solidified (Curve A, fig. 1) no pasty stage occurs. The part first solidified is of the same composition as that still remaining liquid, and the temperature remains constant until the whole is solid.

FIG. 1.



The solidification of an alloy containing 91·66 per cent. of gold and 8·33 per cent. of silver shows similar characteristics,* and remains uniform in composition under all conditions. Having regard to these considerations and to the experience that has been gained of the difficulties attending the preparation of a homogeneous standard silver trial-plate, it seemed more likely that such a plate would be successfully prepared by using a different alloy than by making fresh experiments with silver and copper. The first alloy to be tried consisted of silver 925 parts, gold 75 parts, but although the plates prepared were, doubtless, uniform in composition, the difficulties connected with the assay of the plates were insuperable. It is obvious that the fineness of the plate could not be compared with that of silver coin by the cupellation process, for the reason that the gold would not be separated from the silver in that case. Nor were the wet processes

* 'Roy. Soc. Proc.,' vol. 71 (1903), p. 161.

of assay, which involve dissolution in nitric acid, found to be much more convenient. When the alloy was digested with nitric acid in the ordinary way, at a moderate temperature, large and variable quantities of silver were retained by the gold. When the alloy was boiled in moderately strong nitric acid for 30 minutes, the gold still retained about 0·2 per 1000 of the silver, and a further variable amount was carried off by the vapour rising from the boiling liquid and lost.

It was, therefore, necessary to discover some other alloy which would be at once uniform in composition and easy to use as a standard of comparison.

An examination of the cooling curves of a number of alloys containing 92·5 per cent. of silver afforded evidence that the silver-cadmium alloy would prove to be the most suitable one for trial-plates. Unlike the alloys containing gold, tin, or antimony, the cadmium alloy presents no difficulty in connection with the assay by the ordinary methods, and the cooling curve, B fig. 1, bears a close resemblance to that of a pure metal, the fall in temperature during solidification not being great. The completion of solidification, however, is marked by a slight momentary change of direction of the curve, pointing to the freezing of a small quantity of material of the nature of an eutectic alloy, and it seemed possible that this might correspond to a change in the distribution of the silver throughout the mass, resulting in a lack of homogeneity.

In order to test this, ingots of silver and cadmium of standard fineness were prepared and rolled out. Some difficulties were at first encountered in the melting of the alloy. If pieces of solid cadmium, even when warmed, are added to molten silver, the action is very violent, and varying losses of cadmium by oxidation and volatilisation take place, so that the resulting alloy is seldom of the exact composition required. The method eventually adopted consists in pouring molten silver, heated only slightly above its melting point, into a large crucible containing melted cadmium at a black heat and covered with charcoal. The crucible is then placed in the fire, raised to a bright red heat as quickly as possible, and the alloy well stirred and poured into a closed mould. Under these conditions, when operating with 4 or 5 kilos. of material, the mixing of the metals takes place with comparative quietness, and the loss of cadmium is reduced to about 0·15 per cent. by weight of the alloy. In order to prepare a standard trial-plate, which consists of 925 parts of silver and 75 parts of base metal, it is accordingly necessary to melt 76·5 parts of cadmium and to add 925 parts of silver to it. A large part of the loss appears to take place on the addition of the silver to the cadmium, dense fumes of oxide of cadmium being given off, but on merely melting and re-casting a standard ingot of 5 kilos., the proportion of silver present rises from 92·50 per cent. to about 92·58 per cent.

The silver-cadmium standard alloy is more ductile and is whiter than the corresponding alloy of silver and copper, which has a slightly yellowish tinge. The ingots obtained were 21·5 cm. long, 15·3 cm. wide and 1·25 cm. thick. They were rolled to a gauge of 1·25 mm. and pieces cut from all parts were assayed, with the results that the plates* were found to be practically of uniform composition. The cadmium does not interfere with the ordinary methods of assay, no difference in results due to interference being observable when the trial-plates were compared with pure silver by the Gay-Lussac and Volhard processes of assay. In practice when the fineness of a silver-copper alloy is being compared with that of the trial-plate, by means of the Volhard process, the nitric acid solution of the copper alloy would be coloured blue, while that of the cadmium alloy would remain colourless. This would interfere with the correctness of the comparative final readings, but in order to avoid this difficulty, it is sufficient to add a piece of copper of the appropriate weight to the solution of the cadmium alloy. When the silver-cadmium alloy is cupelled, the cadmium burns off and the loss of silver is about four parts in 10,000 more than if the alloying metal were copper. In comparisons by the cupellation process, it is, therefore, essential that the assay pieces should be made of similar composition by suitable additions of base metals. This course presents no difficulty and in no way detracts from the value of the trial.

The results of these experiments show that trustworthy and convenient trial-plates can be made of silver and cadmium, but it remained to be determined by further study of the properties of the series of alloys whether the uniformity in composition of the trial-plates was fortuitous, or whether it was the inevitable result of its constitution.

The silver-cadmium series has been investigated by Gautier,† who stated that the freezing-point curve consisted of two parts meeting at a point corresponding to the alloy containing about 42 per cent. of silver and that the alloys appeared to consist of isomorphous mixtures of a compound of silver and cadmium with one or other of the pure metals. In order to confirm these observations of Gautier a number of alloys, consisting of silver and cadmium, were prepared and analysed. The silver used for this purpose was purified with the precautions adopted in the preparation of fine "proof" silver in the Mint and was 1000 fine. The cadmium was purchased as pure and was examined for impurities, but none were detected. The proportion of silver in the

* One of the plates was sent to Mr. F. W. Harrold, the Assay Master at the Goldsmith's Hall, and another to Mr. H. Westwood, one of the Assay Masters of the Assay Office, Birmingham. They have kindly made a number of assays on the plates, and state that the composition of each plate is uniform.

† 'Bull. de la Soc. d'Encouragement,' Fifth Series, I, p. 1315 (1896).

alloys was determined by the Volhard process of assay. Cooling curves were taken of the alloys by means of a Le Chatelier thermocouple and the recording pyrometer described by Roberts-Austen* and the following results were obtained :—

Freezing-points of the Silver-Cadmium Alloys.

Percentage of silver by weight.	Atomic percentage of silver.	Freezing-points.
100·0	100·0	961°5
95·01	95·18	956·5 (920°)
92·63	92·87	948 (916)
92·57	92·81	945 (913)
88·80	89·16	918 (889)
87·20	87·60	907 (865)
84·59	85·07	895 (858)
83·34	83·84	893 (854)
79·94	80·50	854
74·98	75·65	818
66·10	66·80	810
63·83	64·64	795 (718)
57·74	58·62	720 (695)
54·39	55·27	720 (424)
51·39	52·28	720 (430)
49·36	50·27	694 (419)
41·68	42·57	665 (619)
39·85	41·26	676 (643)
30·11	30·88	(590°) 571
29·52	30·27	(586) 569
21·12	21·74	446 (338)
9·12	9·42	(446) 332
1·20	1·22	315
0·60	0·61	320
0·0	0·0	323

The temperatures in brackets denote subsidiary freezing points which are generally below but sometimes above the main freezing points.

The curve of equilibrium between liquids and solids of the series is given in fig. 2. It has been plotted from the results given in the table. The upper continuous line is the liquidus curve. The solidus curve, which is not complete, is represented by the lower line, and is based on a study of the cooling curves, and of the micro-structure of chilled specimens.

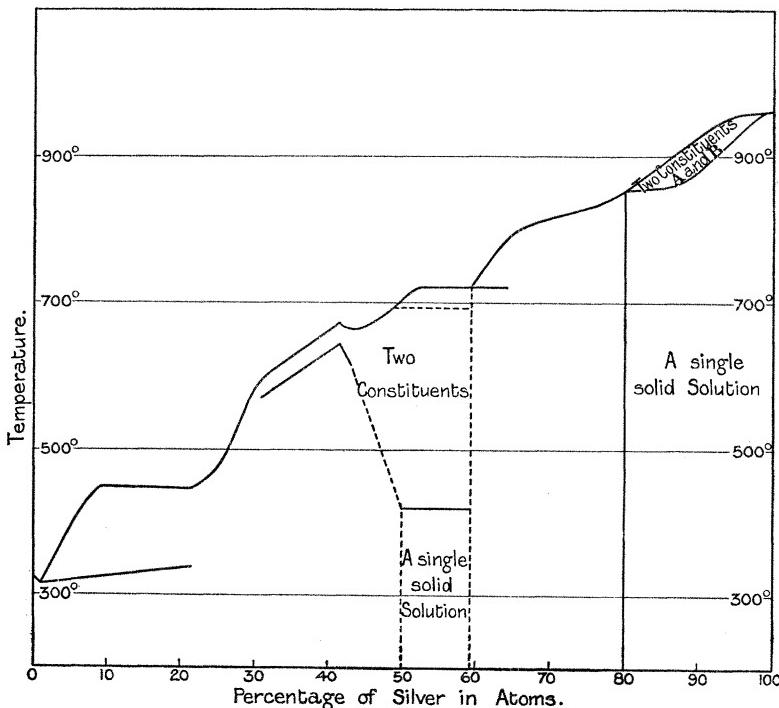
When alloys containing more than 80 per cent. of silver† are

* 'Inst. Mech. Eng. Proc.,' Oct., 1891, p. 543.

† Both here and subsequently "per cent." is used for "number of atoms per cent." It happens, however, that this is nearly the same as the percentage by weight, the atomic weights of silver and cadmium differing but little.

allowed to cool at a moderate rate, the greater part of the mass solidifies at a definite temperature, leaving a very small part only to solidify at a lower temperature. The final freezing point is marked by a minute but distinct check in the rate of cooling. It becomes less marked as the percentage of silver falls below 95 per cent., and disappears altogether before the 80-per-cent. alloy is reached. The 80-per-cent. alloy itself solidifies nearly as a whole, and its cooling curve resembles that of a compound, or a pure metal. There is little

FIG. 2.—Curves of Equilibrium of Silver and Cadmium.



doubt that ingots 800 fine in silver would be uniform in composition. As the percentage of silver falls from 80—65 per cent., the initial freezing or liquidus point becomes of less importance, and the pasty stage more pronounced and of longer duration.

The alloys containing about 66 per cent. of silver and approximating in composition to that required by the formula Ag_2Cd are somewhat less ductile than those members of the series which are richer in silver. They are more readily attacked by nitric acid than the alloys containing either more or less silver. This points to a lack of homogeneity, a conclusion that is supported by the shape of the cooling curve

of the 64·64-per-cent. alloy. There is here a long pasty stage between the initial freezing point at 795°, and a second point at about 718°. During this range of temperature the slowness of the rate of cooling shows that solidification proceeds continuously and that the part of the mass remaining liquid undergoes a continuous change in composition. At the point when solidification is completed there is a more pronounced evolution of heat at about the same temperature as that at which solidification begins in the alloys containing from 52—58 per cent. of silver. The liquidus curve appears to show a small cusp corresponding to the compound Ag_2Cd , but it is probable that the compound Ag_2Cd , which was detected by Heycock and Neville in solution in other metals* is partly or entirely dissociated when melted by itself.

The alloy containing 58·62 per cent. of silver has two freezing points at 720° and 695°, separated by a pasty stage. The alloys containing from 52—55 per cent. of silver have freezing points at 720° and 420°. The eutectic solidifying at 695° was not observed in the cooling curves of these alloys, although there is little doubt that it must exist, particularly in view of the micro-structure. The 50-per-cent. alloy solidifies at 694°, and shows the eutectic point at 420°.

In the series containing from 50—60 per cent. of silver, the pasty stage succeeding the initial freezing point gradually diminishes as the percentage of silver is reduced, until in the 50-per-cent. alloy the fall of temperature during solidification is only about 20°, whereas in the 75-per-cent. it is nearly 100°. Nevertheless the freezing point of the 50-per-cent. alloy is not so sharp as that of an undisassociated compound, and after the temperature has fallen at a normal rate to about 420° another considerable evolution of heat takes place, during which the temperature remains stationary. The point is also observable in the cooling of the 52-, 55-, and 58-per-cent. alloys, becoming successively smaller and dying away at about the 60-per-cent. alloy. Prolonged heating at various temperatures between 420° and 695° had not any apparent effect on the specimens, which retained their shape when not subjected to stress. When, however, a cast bar with composition corresponding to the formula AgCd was subjected to a bending stress equal to 10 grammes per square millimetre of cross section (about 14 lbs. per square inch), it was found to become suddenly plastic and to bend almost double without cracking at a temperature of 450°. When chilled at temperatures somewhat above 420° the specimens assumed a red or lilac tint, especially after light polishing, which is not so markedly observable in the specimens chilled from below 420°. The colour is observable in all the alloys containing from 40—50 per cent. of silver, and is always confined to the surface layer. The

* "The Freezing-point of Triple Alloys," 'Chem. Soc. Trans.,' vol. 65 (1894) p. 65.

similar case of the silver-zinc alloy AgZn has been investigated by Heycock and Neville,* who also refer to the colour of the alloy AgCd.

The cooling curves of some alloys containing about equal numbers of atoms of silver and zinc were also prepared for comparison, and were found to be very similar to the cooling curve of AgCd. The freezing point of the alloy containing 51 atoms of zinc to 49 atoms of silver is at 693°, and the evolution of heat by the alloy in the solid state is at 281°. The corresponding temperatures in the case of the alloy containing equal numbers of atoms of silver and zinc were found to be 690° and 271°. These results can be correlated with the facts observed by Heycock and Neville, who showed that the silver-zinc alloy could be made to assume a red tint if heated to a temperature near 300°, the lowest effective temperature being 285°, and suddenly chilled. The disappearance of the red tint thus appears to coincide with an evolution of heat in both cases. The red tint can also be obtained in either case by abrasion. It is well shown in filings and sometimes in polished specimens.

The liquidus curve of the silver-cadmium alloys shows a well-marked cusp at about the 40-per-cent. alloy, pointing to the existence of the compound Ag_2Cd_3 . This alloy is hard and excessively brittle, breaking with a conchoidal fracture, a proof of homogeneity of structure.

The remainder of the freezing point curve is of an ordinary type, consisting of two branches meeting at a minimum at about the alloy containing 1·2 per cent. of silver, which solidifies at 315° or 8° below the freezing point of pure cadmium.† Further additions of silver raise the freezing point until a maximum of 676° is reached at the 40-per-cent. alloy. A branch of the curve of equilibrium was observed containing about 10 per cent. of silver solidifying at 332°.

The liquidus curve is thus seen to consist of 7 parts, which are as follows :—

- (1) Between pure silver and the compound Ag_4Cd , convex upwards. The two constituents appear to be isomorphous.
- (2) Between the compounds Ag_4Cd and Ag_2Cd , concave upwards.
- (3) Between the compounds Ag_2Cd and Ag_3Cd_2 . Nearly a straight line with a horizontal branch corresponding to the freezing point of the compound Ag_3Cd_2 .
- (4) Between the compounds Ag_3Cd_2 and AgCd , there is a horizontal branch corresponding to the freezing point of the compound Ag_3Cd_2 . There is also probably another corresponding to the freezing point of the

* 'Camb. Phil. Soc. Proc.,' vol. 9, Pt. 4, 1896.

† Rudberg ('Poggend. Annal.,' vol. 71, 1847, p. 460) and Riemsdijk ('Archives Néerlandaises,' vol. 3, 1868, p. 29) both gave the melting-point of cadmium as 320°, and Gautier (*loc. cit.*) takes it as 322°. The temperature of 323° adopted here was determined by comparison with the melting-point of pure lead, which was taken as 326°.

compound AgCd , and a third corresponding to the freezing point either of the compound AgCd_3 or of a eutectic alloy consisting chiefly of this compound.

(5) Between the compounds AgCd and Ag_2Cd_3 . A curve concave upwards.

(6) Between the compounds Ag_2Cd_3 and AgCd_3 .

(7) Between AgCd_3 and cadmium. A curve with a distinct minimum at about 1·2 per cent. of silver. There are two horizontal branches, one due to the solidification of a eutectic of this composition, and the other to the freezing of the compound AgCd_3 .

Micro-structure of the Alloys.

The alloys containing upwards of 80 per cent of silver all present similar characteristics. Their structure is well developed on polished surfaces by dipping them for a few seconds in hot nitric acid of a specific gravity 1·25. Slowly cooled specimens, in which the solidification occupies about 5 minutes and the subsequent cooling to a low red heat about half an hour, are seen to consist of crystallites of a silver-rich body set in a darker coloured matrix which has been more deeply etched by the acid than the crystallites (see fig. 3, Plate 10). The limiting case of pure silver shows no matrix and the crystallites are large, the crystal grains in small specimens being from 5—8 mm. in diameter. Similarly no matrix was observed in the alloy containing 97·3 per cent. of silver but it was detected in the 95-per-cent. alloy, and showed some increase as the silver diminished to 80 per cent. At the same time the size of the crystallites diminished to a diameter of about 1 mm. When these alloys were re-heated for from 1—4 hours at temperatures intermediate between the initial freezing point and the "eutectic" point referred to above, the crystal grains broke up and a fine network of the dark-coloured matrix was formed. When reheated at any temperature above a red heat but below the final solidification point, the matrix disappeared and crystals were formed occupying the whole area of the field. The higher the temperature (below this point) and the longer the time during which it was maintained, the larger the crystals grew and the straighter and more regular became their bounding faces. All the specimens were chilled after re-heating.

It appears, therefore, that at all temperatures below the solidus curve, these alloys are homogeneous, consisting of a single solid solution, doubtless consisting of varying proportions of silver, and the compound Ag_4Cd the existence of which has been referred to by Heycock and Neville.* These two substances, silver and Ag_4Cd , must be regarded as isomorphous. It follows that the more slowly these alloys are cooled,

* "The Freezing-point of Triple Alloys," "Chem. Soc. Trans.," vol. 65 (1894), p. 65.

the more uniform the composition should be. It should be possible to prepare perfectly uniform alloys of any composition containing more than 80 per cent. of silver by re-heating them to about 850° for a number of hours. A practical difficulty in carrying this out would be that the cadmium would be partly volatilised, so that it would be necessary to remove the outer layers of the ingots after heating them.

On the other hand, Osmond has pointed out that it is by no means uncommon for crystallites to be developed by the attack of suitable re-agents in media which are chemically homogeneous. He cites the bronzes and the gold-copper alloys as instances. According to this view the specimens showing crystallites are already uniform in composition and do not require to be annealed in order to become so. It is to be observed, however, that the gold-copper alloys have been shown to be non-homogeneous.* Osmond does not state to what bronzes he refers, but the copper-tin alloys are now well known to be heterogeneous also. It may be repeated that in practice the 92·5-per-cent. alloy is found, on casting, to be uniform in composition, so that it is unnecessary to anneal it.

In the alloys containing from 80—70 per cent. of silver, the crystallites in slowly cooled specimens are larger and more regularly cross- or fern-shaped than in those with more silver (see fig. 4, Plate 10). The matrix is readily dissolved out by nitric acid, leaving the crystallites in relief surrounded by a deep-sunk network. The area occupied by the crystallites is reduced, and that occupied by the matrix increased as the percentage of silver falls. The equilibrium of the systems at lower temperatures has not been examined in this part of the series.

The alloy corresponding to the formula Ag_3Cd is much finer grained than either the 64- or the 70-per-cent. alloy. Etching with nitric acid leaves an excessively fine network in relief with darker pittings between, but no regular structure is observable. Other reagents are equally ineffective in developing the structure. Re-heating at 750° for $1\frac{1}{2}$ hours, and subsequent chilling, merely increases the size of the network without in any other way changing its appearance. One curious effect of heating to 750° these specimens embedded in sand is that the cadmium on the surface is volatilised, leaving a layer of pure silver. On removing this during the operation of polishing, a black layer is encountered coloured by oxide of cadmium, and underneath this the original alloy is found to exist. The layers are not everywhere of the same thickness, so that in the course of polishing alternate rings of white and black are produced, resembling the well-known Japanese decorative metal-work known as Mokumé, which is used in jewellery.

The cooling curves indicate that the compound Ag_3Cd_2 separates

* Roberts-Austen and Rose, 'Roy. Soc. Proc.,' vol. 67 (1900), p. 105.

from the alloys containing between 50 and 60 per cent. of silver, and this is borne out by the micro-structure. The alloys when rubbed with potassium cyanide solution are seen to consist of white oblong crystals set in a red-coloured matrix (see fig. 5). As the percentage of silver diminishes the area covered by the crystals is reduced, and the amount of matrix increases. The white crystals evidently consist of the compound Ag_3Cd_2 , and the red matrix of AgCd .

The alloys containing between 50 and 40 per cent. of silver are remarkable for resisting the attack of the ordinary etching reagents. Nitric acid has little effect on them, but they are slowly dissolved by hot acid of a specific gravity of 1.3 without their structure being revealed. A similar lack of success attended the use of sulphuric and hydrochloric acids, of soluble sulphides, of alkaline sulphides with the aid of a galvanic battery, and of heat with free exposure to the air. The alloys are not affected by ammonium sulphide under conditions in which silver-copper alloys or pure silver are instantly tarnished. The structure was developed by a polish attack, which consisted in rubbing the polished specimens on parchment with fine alumina moistened with a solution of 0.5 per cent. of cyanide of potassium. The action is partly abrasive, the red colour being strongly developed in some of the crystals. In the 50-per-cent. alloy, slowly cooled specimens are seen to consist of large crystals of 2—3 mm. in diameter. There is no cementing material, and the crystals are distinguishable from one another under low powers only by their shades of colour. Under high powers (above 1000 diameters) the most strongly coloured crystals are seen to be covered with a number of minute irregular pits and short trenches, which are bright red, the space between being colourless. The difference between the crystals seems to be only that of the orientation of the particles forming them, so that the surface of some crystals is more readily abraded than that of others. The structure, however, is not readily revealed without the aid of the cyanide solution. The abrasions form an irregular network, which gives some of the crystals a minutely cellular appearance, visible at a magnification of 50 diameters. In quickly cooled cast specimens the crystals are much smaller, few being more than 0.3 mm. in diameter, and traces of a hard white cement are discernible between the crystals.

The same alloys when re-heated to 350° for 6 hours and chilled show an even more minute structure, the crystals being only about 0.02 mm. in diameter (see fig. 6). A few hard white projecting grains, probably existing in the alloy after casting and before reheating, are visible under a magnification of 1800 diameters on a slightly pink ground consisting of a solid solution of AgCd and Ag_2Cd_3 .

When the 50-per-cent. alloy is heated for 6 hours above 420° and chilled, the separation of the two constituents is far more complete. The alloy is now made up of large bright red hexagonal crystals about



Fig. 3. Silver 92.87%
Cadmium 7.13%
 $\times 50$ vert.



Fig. 4. Silver 80.5 %
Cadmium 19.5 %
 $\times 10$ oblique.

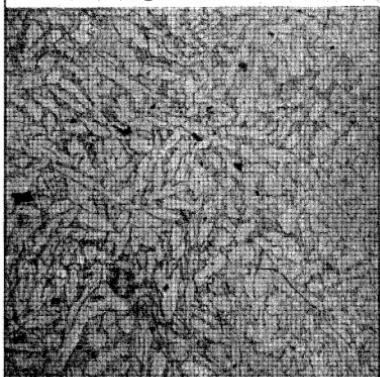


Fig. 5. Silver 55.27%
Cadmium 44.73%
 $\times 20$ vert.

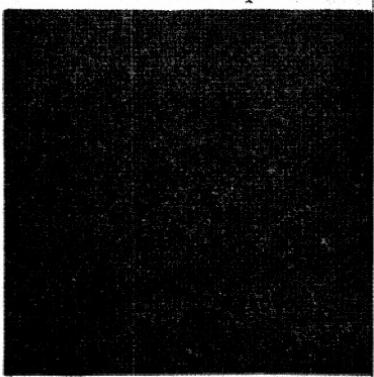


Fig. 6. Silver 50.70% Cadmium 49.30%
Quenched from 350°
 $\times 10$ oblique.

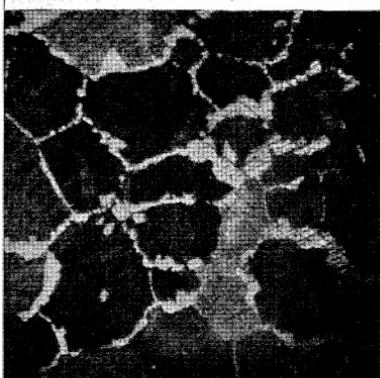


Fig. 7. Same as Fig. 6.
Quenched from 550°
 $\times 30$ vert.

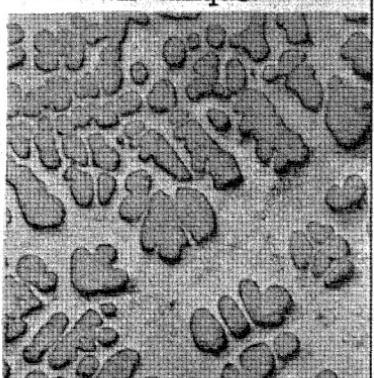


Fig. 8. Silver 94.2%
Cadmium 9.58%
 $\times 50$ vertical.

1 mm. in diameter. Near the outside of the specimens these crystals occupy the whole area, but towards the centre the hard white alloy is segregated, forming a cement between the red crystals (see fig. 7). It seems clear that these two constituents are separated at temperatures above 420° , and that the white constituent fuses at that temperature. The white constituent is readily attacked by nitric acid, and may be the compound AgCd_3 .

The 40-per-cent. alloy, when slowly cooled, is homogeneous and consists of small crystals, about 0.3 mm. in diameter, which become more regular hexagons when re-heated for 24 hours at 350° and chilled, and also when heated at 570° and chilled, but do not increase in size. The alloy remains homogeneous under these conditions, and evidently consists of the compound Ag_2Cd_3 .

The portion of the series between the 40- and the 25-per-cent. alloys consists of hard slightly pinkish crystallites of Ag_2Cd_3 , set in a matrix which approximately corresponds in composition to AgCd_3 . The alloys can be etched with nitric acid, and the unattacked crystallites, at first forming almost the whole of the mass, become somewhat rare in the 30-per-cent. alloy, and disappear altogether before the 25-per-cent. alloy is reached.

Specimens containing less than 25 per cent. of silver are much more rapidly attacked by nitric acid than those richer in silver, and when corrosion takes place it is a magma of cadmium with very little silver that is attacked and darkened, leaving the harder white crystallites of AgCd_3 practically untouched (see fig. 8). The structure is developed when sections are merely polished, the crystallites of AgCd_3 standing out in relief. They diminish in number as the percentage of silver is reduced.

The results of the investigation may be summarised as follows:—

(1) Evidence is afforded of the existence of the compounds AgCd_3 , Ag_2Cd_3 , AgCd , Ag_3Cd_2 , Ag_2Cd , and Ag_4Cd .

(2) The alloys containing from 0—25 per cent. of silver consist, when solid, of crystals of AgCd_3 set in a matrix of cadmium. Those containing between 25 and 40 per cent. of silver consist of the compound Ag_2Cd_3 set in a matrix consisting mainly of AgCd_3 . The alloy containing about 50 per cent. of silver consists of crystals of a silver-rich body set in a matrix consisting chiefly of AgCd_3 . The matrix or eutectic solidifies at 420° , or nearly 300° below the freezing point of the crystals.

The alloys containing from 50—60 per cent. of silver consist, at temperatures above 420° , of mixtures of two different solid solutions, one of which is chiefly composed of the compound AgCd , and the other of Ag_3Cd_2 . Traces of the eutectic freezing at 420° are still visible.

When more than 80 per cent. of silver is present, the alloys consist of a mixture of two bodies at temperatures between the liquidus and

solidus curves, but these unite to form a single solid solution at points on the solidus curve.

(3) The alloys containing over 80 per cent. of silver do not undergo segregation under ordinary conditions, and are practically homogeneous and uniform in composition. They are well suited as a material for the manufacture of trial-plates.

"On the Wetting of Cotton by Water and by Water Vapour."

By ORME MASSON, D.Sc., F.R.S. Received April 25, 1904.

Introduction.

If two thermometers, one of which has its bulb protected by a close covering of ordinary cotton wool, be simultaneously immersed in the same water, all being originally at the same temperature, the protected thermometer shows a marked rise, while the naked one undergoes no perceptible change. Heat is, therefore, generated locally by the wetting of the cotton covering.

The maximum temperature is reached in 2 or 3 minutes, after which there is a fall, the rate of which steadily diminishes in a characteristic manner, so that, when all necessary precautions are taken, a difference of temperature between the cotton and the surrounding water is still distinctly perceptible after several hours. Both the extent of the rise and the rate of the whole change depend on several conditions. With a given thermometer the most important factors are the quantity of cotton wool, its initial condition with respect to hygroscopic moisture, and the temperature of the water. Other things being equal, the effect is more marked with a large covering than with a small one and at a higher than at a lower bath temperature, but the previous condition of the cotton is a more important factor than either. If taken in its ordinary state after exposure to the air of the laboratory, when it usually contains about 8 or 9 per cent. of moisture, it may show a rise of 2° or 3° C., but if precautions be taken to insure that it is dry at the moment of immersion in water (at its own temperature), the same sample will show a rise of from 8—12° or more.

The relatively large amount of air which is always entangled within the cotton wool does not escape during or after immersion, and the bundle presents a glistening appearance under water which suggests that it is not completely wetted. That this fact is important in connection with the observed temperature change is shown by the behaviour of the so-called "medicated" or "absorbent" cotton wool, which differs from the ordinary (nearly pure) material in having been freed by solvents from traces of natural cotton wax. This gives a



Fig. 3. Silver 92.87%
Cadmium 7.13%
 $\times 50$ vert.



Fig. 4. Silver 80.5 %
Cadmium 19.5 %
 $\times 10$ oblique.

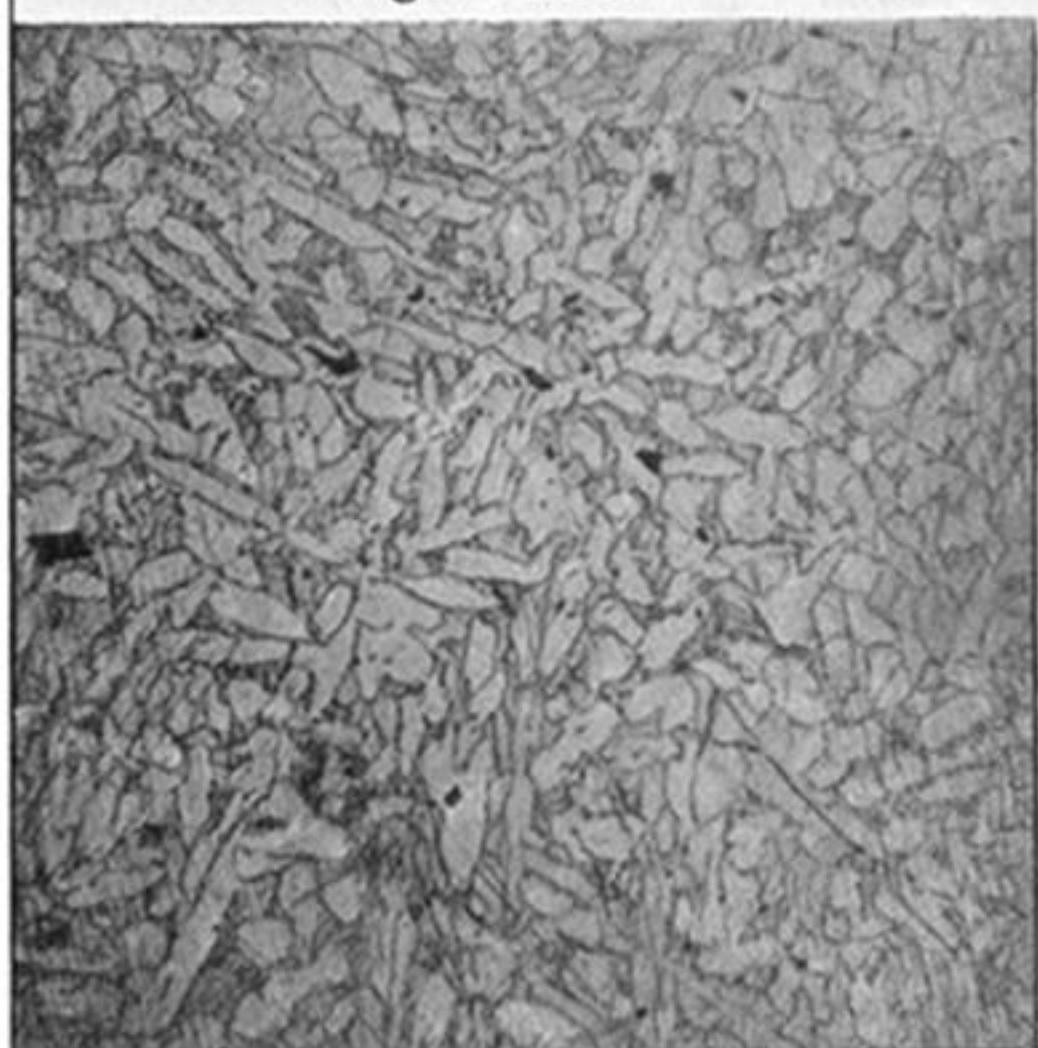


Fig. 5. Silver 55.27%
Cadmium 44.73%
 $\times 20$ vert.

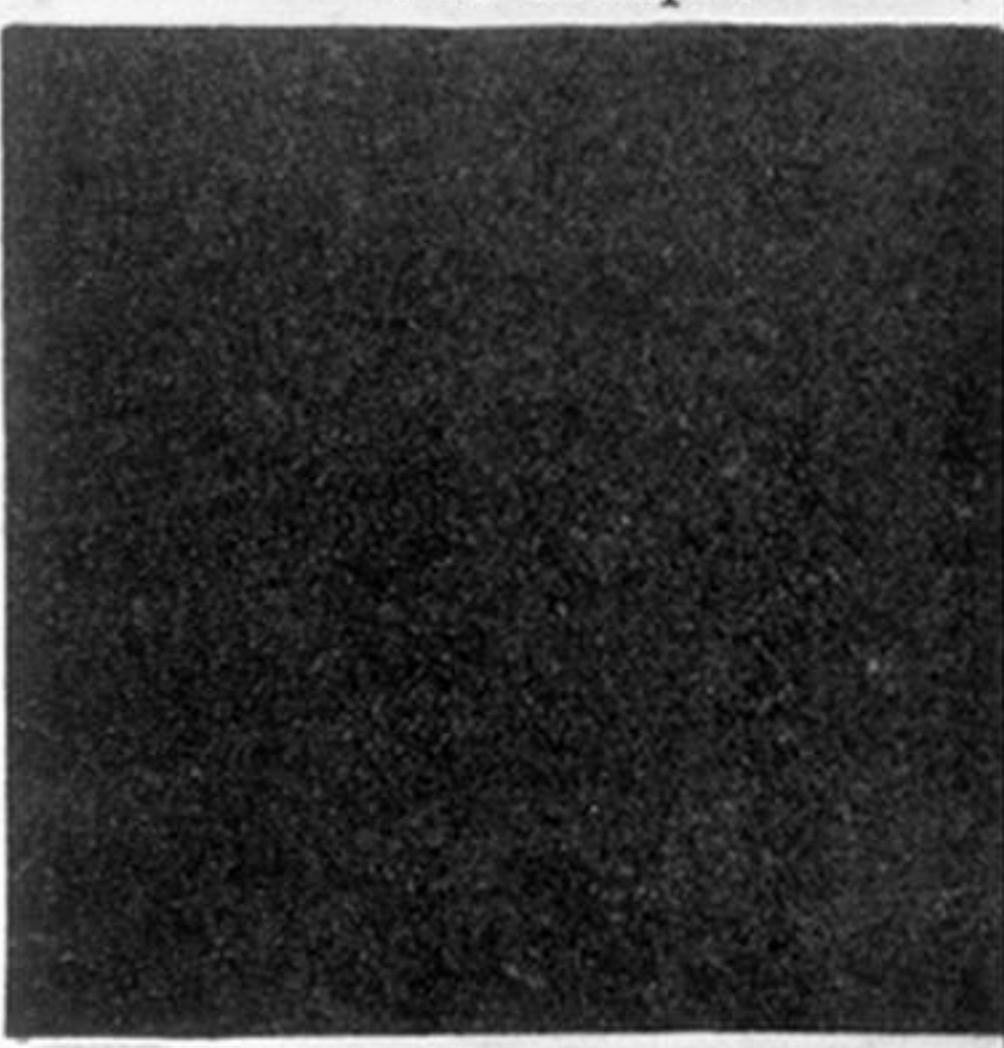


Fig. 6. Silver 50.70% Cadmium 49.30%
Quenched from 350°
 $\times 10$ oblique.

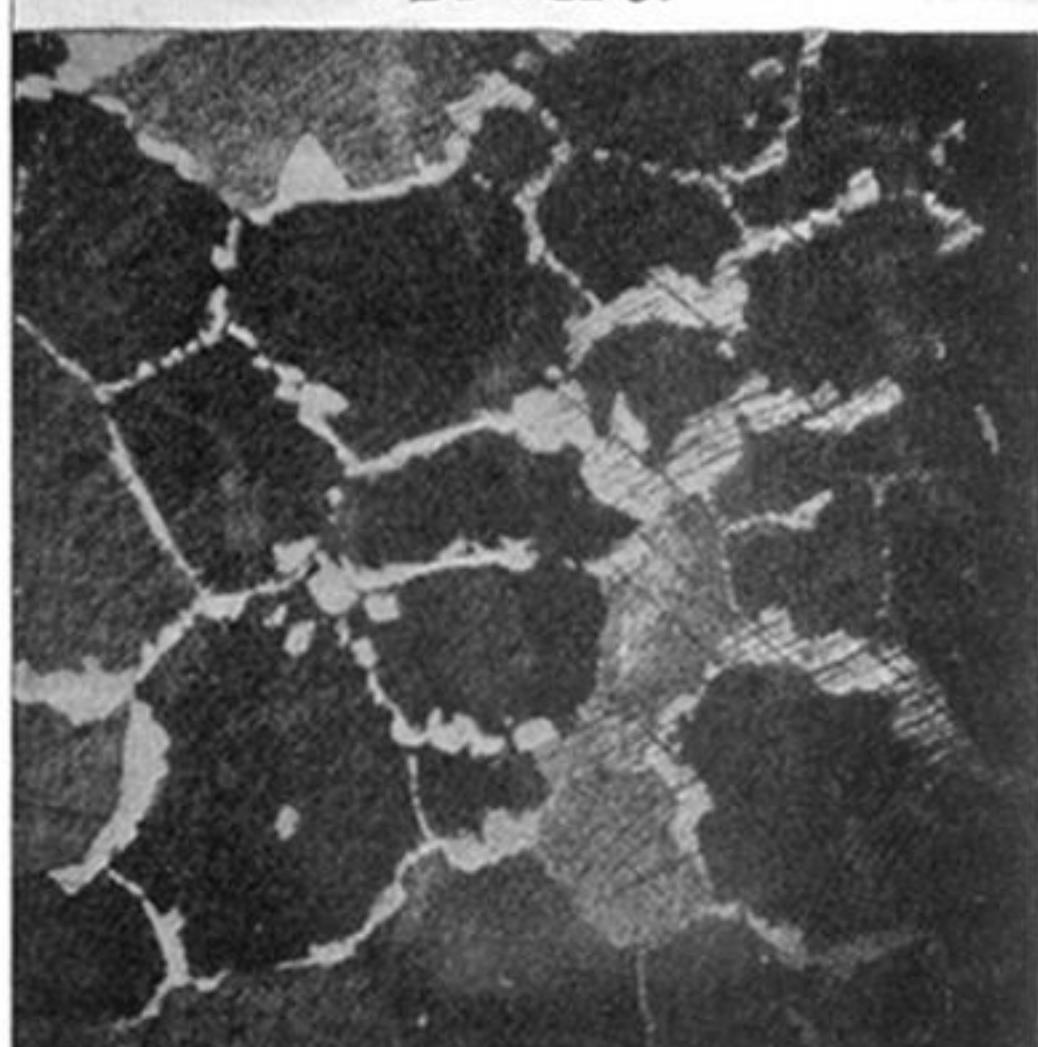


Fig. 7. Same as Fig. 6.
Quenched from 550°
 $\times 30$ vert.

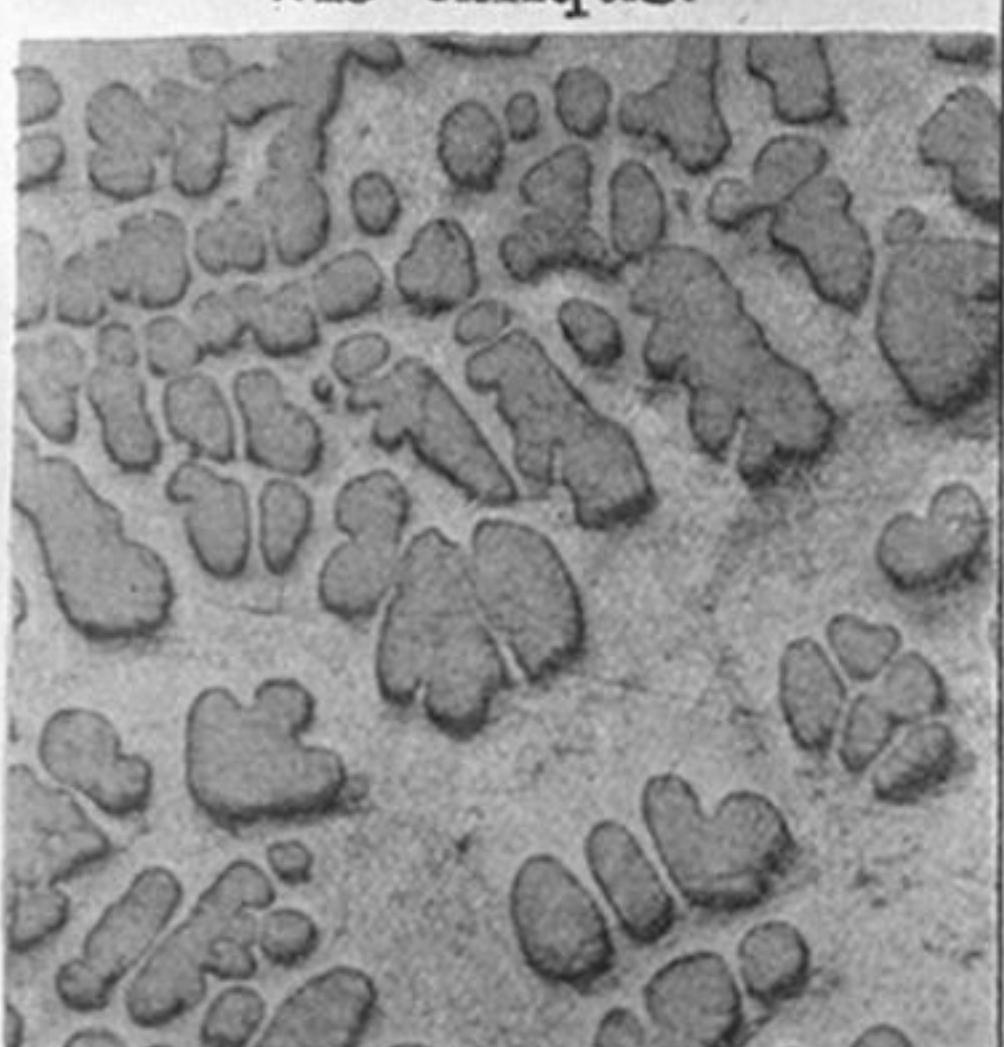


Fig. 8. Silver 9.42%
Cadmium 90.58%
 $\times 50$ vertical.